

PATENT SPECIFICATION

NO DRAWINGS

891944



Date of Application and filing Complete Specification Aug. 18, 1959.

No. 28223/59.

Application made in United States of America on Aug. 19, 1958.

Application made in United States of America on July 31, 1959.

Complete Specification Published March 21, 1962.

Index at acceptance:—Classes 2(6), P2D1X, P2T(1H:2X), P4D(2:3:B1), P4K7, P4T(1H:2X), P7D(1A:1X:2A1), P7K(4:7), P7T(1H:2X), P8D(2A:3A:3B), P8T(1H:2X), P10D(1A:1X:2A), P10T(1H:2X), P11P(4:5), P11T(1H:2X), P12; and 96, B(1:2A:2B:6:11B:13I:13X:20:24).

International Classification:—C08f. D21h.

COMPLETE SPECIFICATION

Improvements relating to Artificial Shaped Structures

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to artificial shaped structures, and more particularly to structures comprising spongy and reticulated fibres produced from synthetic organic fibre-forming polymers.

In accordance with the invention, a novel and useful product is provided by a process wherein a plexifilament (as defined below) produced from a synthetic organic fibre-forming polymer, while in intimate contact with an organic modifier, is subjected to ionising radiation to produce chemical bonds between the plexifilament and the organic modifier. More specifically, an organic modifier is applied to the surface of the plexifilament or, for deep-seated modification, is permitted to diffuse into the substrate, and the structure is thereafter irradiated with ionising radiation to induce chemical bonding. Alternatively, the organic modifier, especially when it is of high molecular weight, may remain upon the surface of the plexifilament substrate during the irradiation step, thus producing a uniform coating chemically grafted to the polymer substrate. The organic modifier may be polymeric or may polymerise in the process, or it may be a non-polymerisable compound.

The plexifilament structure is a three-dimensional fibrous integral plexus of the synthetic organic fibre-forming polymeric material. Within the framework of this structure, plexi-

filaments may have properties varying over a wide spectrum; but, in general, a plexifilament comprises a multitude of fibrillous strands or sections which intermittently unite and separate at random intervals both longitudinally and transversely to form a continuous three-dimensional integral fibrillous plexus ranging in appearance from that of an elongated matted cobweb to that of a slick continuous filament yarn, and which in some instances has the exterior of a monofilament yarn even though the interior is always a three-dimensional integral fibrous plexus as described above.

In one form, the plexifilament contains a labyrinth of innumerable fine (small in cross section) longitudinal tunnels which may interconnect at random intervals, and in another but closely related form it does not contain tunnels, but is honey-combed with a multitude of longitudinally elongated cavities, or it may contain both tunnels and cavities. In all cases, these tunnels or cavities or both are distributed throughout the strand both longitudinally and transversely to provide the unitary fibrous plexus. On working such a plexifilament, hereinafter referred to as a "foamy" plexifilament, as by drawing, twisting or pressing, cavities present may collapse with considerable popping noise.

In another form, the plexifilament is substantially free of tunnels and/or cavities and is characterised by a plurality of fibrils which unite and separate at random longitudinal and cross-sectional intervals throughout the strand to provide a three-dimensional unitary network or web in which all elements are integral with each other, thus resembling a staple fibre yarn without loose ends.

The term "fibrous", as used herein, is intended to include individual and distinct strands characterised by a length many times

[Price 4s. 6d.]

greater than the greatest transverse dimension as in an ordinary staple fibre. These distinct strands are termed herein as "fibrils" and, of course, differ from the staple fibres in an ordinary staple yarn in that in a plexifilament the ends of a "fibril" are normally integral with the ends of other fibrils so that the whole plexifilament is unitary with the fibrils combining and separating at random longitudinal and cross-sectional intervals. The term "fibrous" is also used in the sense that a sponge or a paper is fibrous, and thus includes the partitioning structures in plexifilaments which are perforated with tunnels or which contain numerous closed cavities throughout. The fibrous character of all plexifilaments is readily apparent from the fact that all are much more resistant to tearing or breaking transversely than to splitting lengthwise, showing that in both fibrillous plexifilaments (those containing substantially all fibrils and few, if any, tunnels or cavities) and in foamy or spongy plexifilaments containing a multitude of tunnels, cavities or both and substantially no fibrils, the polymeric material is distinctly fibrous in structure, and the fibres in plexifilaments are oriented longitudinally. Further evidence lies in the observation that fibrils in plexifilaments are also longitudinally oriented as are elongated tunnels and/or elongated cavities when present.

In general, tunnel and cavity walls and fibrils throughout a plexifilament have a thickness of less than about 2 microns and preferably less than 1 micron.

The plexifilaments are thus yarn-like strands having the beneficial properties of both staple fibre yarns and continuous filament yarns. These strands have the bulk of staple fibre yarns but are substantially entirely without loose ends, and like continuous filament yarns have high strength even at zero twist. Plexifilaments are unlike both staple and continuous yarns in being unitary and no twist is necessary to hold a plexifilament together. Further information regarding plexifilaments will be found in our Specification No. 18582/58 (Serial No. 891,943).

The term "synthetic fibre-forming polymer" denotes both condensation and addition polymers. By the term "synthetic organic condensation polymer" is meant a polymer which can be formed by polymerisation with elimination of small molecules such for example as HCl, H₂O, NaCl and NH₃, including those polymers which on chemical degradation yield monomeric end products differing in composition from the structural units (J. P. Flory, "Principles of Polymer Chemistry", Cornell Univ. Press, Ithica, N.Y.). These polymers are also characterised by their ability to hydrolyse to a monomer. Another characteristic which distinguishes condensation polymers (for instance, from addition polymers) is that the repeating

units which form an integral part of the polymer chain are linked by other than carbon-to-carbon bonds. Among such polymers may be mentioned polyamides, polyureas, polyurethanes, polyesters, polyoxymethylenes, polyethers (epoxy polymers), polyacetals and polysulphonamides, and copolymers of such materials. The preferred condensation polymers are those which are substantially linear, i.e. those which are produced from predominantly difunctional reactants.

By the term "synthetic addition polymer" is meant a polymer which can be formed by vinyl polymerisation, i.e. polymerisation which proceeds by combination of an unsaturated monomer with itself or with other unsaturated monomers by linkage at the olefinic bonds. Among suitable monomers for such polymerisation may be mentioned styrene, the acrylic acid esters, vinyl chloride, vinylidene chloride, vinyl acetate, the vinyl ketones, the vinyl ethers, the halogen-, sulphur-, nitrogen- and phosphorus-containing vinyls, the vinyl silanes, ethylene, propylene, the allyl esters, acrylonitrile and methacrylonitrile. Linear, branched, isotactic and atactic polymers are suitable. The term comprehends copolymers as well as homopolymers. These polymers are comprehensively discussed by Flory in ("Principles of Polymer Chemistry", Cornell Univ. Press, Ithaca, N.Y. (1953)). The preferred addition polymers are those which are substantially linear, i.e. those which are produced from predominantly monoethylenically unsaturated monomers; however, branching may be present.

By "grafted polymer" is meant a polymer which is modified, after polymerising and shaping, by chemically bonding thereto molecules of a chemically dissimilar organic compound.

By "irradiation" is meant the process by which energy is propagated through space, the possibility of propagation being unconditioned by the presence of matter, as distinguished from mere mechanical agitation in a material medium such as is characteristic of energy produced by a sonic or ultrasonic transducer, although the speed, direction and amount of energy transferred may be thus affected.

By "ionising radiation" is meant radiation having sufficient energy to remove an electron from a gas atom, forming an ion pair; this requires an energy of about 32 electron volts (ev) for each ion pair formed. This radiation has sufficient energy to break chemical bonds non-selectively; thus, in round numbers radiation of energy 50 ev and above is effective for the process.

By an "organic compound" is meant a compound in which a carbon atom is attached only to one or more of the following: hydrogen, halogen, nitrogen, oxygen, sulphur, a radical containing a nitrogen, oxygen or sulphur atom through which the radical is

attached to the carbon atom, or an organic radical, with the proviso that it may not be doubly bonded to more than one sulphur or oxygen atom (i.e. the compounds CS_2 , CO_2 and COS are excluded). By "organic radical" is meant a radical predominantly hydrocarbon except for the presence of atoms or radicals immediately hereinbefore listed. Where one or more of the said atoms or radicals is an organic radical it is preferred that it be linked to the carbon atom originally referred to by a carbon-to-carbon bond.

Typical compounds included are hydrocarbons, alcohols, acids, ethers, ketones, esters, aldehydes, isocyanates, sulphonates, mercaptans, thioethers, disulphides, nitriles, nitro compounds, amines, amides and halides. Compounds with ethylenic unsaturation are especially preferred, since a minimum radiation dose is required to graft a given weight of modifier.

However, surprisingly, it has been found that non-polymeric organic compounds (free from aliphatic unsaturation) are also readily grafted, to produce effective modification of polymer properties. Of these compounds the chain transfer agents are preferred.

Another useful class of modifiers are the high molecular weight compounds, especially polymers.

The plexifilaments employed in the process of the present invention may be produced by "flash spinning" a homogeneous solution comprising a synthetic fibre-forming polymer in an organic liquid which is a solvent for the polymer at the elevated temperature employed, as described in Specification No. 18582/58 (Serial No. 891,943). The solution may be extruded from a vessel maintained at a temperature above, preferably at least $40^\circ C$. above, the normal boiling point of the organic liquid and at superatmospheric pressure, through a spinneret containing one or more holes, into a medium at a lower pressure, preferably air at normal atmospheric pressure. The pressure in the vessel may be autogenous or higher. The temperature and pressure in the extrusion vessel should be sufficiently high so that most of the solvent is flashed off immediately the pressure on the confined solution is released by opening a valve forming part of the spinneret assembly and located ahead of or behind the orifice. Extremely high spinning speeds are attained, normally above about 5000 ypm per orifice. Productivity of about 13,000—15,000 yards of filamentary material per minute per hole are obtainable.

Flashing-off of solvent during the spinning process is much like the flash evaporation of solvent in well-known flash distillation procedures. The rapid and substantial reduction in pressure upon the confined polymer solution when the extrusion orifice is opened results in an almost violent escape of solvent, causing multitudinous longitudinal ruptures of

extruded polymer and resulting in the production of the integral fibrous plexus, ranging from a completely fibrillous plexus at one extreme to a porous, longitudinally extended tunnel-containing yarn-like bulky foamy strand at the other. It is surprising that, despite the violent nature of the process, indefinitely continuous strands are obtained.

It is important that the polymer solution to be extruded contain at least 5% of polymer by weight. If the concentration of polymer solution is too low for the particular spinneret assembly used, the polymer extruded is blown apart and the continuous product is not obtained. If in the same assembly the solution temperature is too high, the extruded polymer may be fused or blown apart depending on the thermal properties of the solvent. Conversely, if the polymer solution concentration is too high or the temperature of the solution in the extrusion vessel is too low for the particular spinneret assembly used, a foamy, non-fibrillous product is obtained. It is also important that the polymer solvent utilised have a boiling point substantially lower than the melting point of the polymer and possess a substantial vapour pressure at the extrusion temperature if the plexifilament structure is to be produced.

The material of the ungrafted plexifilament may for example be hydrocarbon polymers, such for instance as polyethylene and polypropylene, poly(isobutyl ethylene), or ethylene copolymers, for example with alkenes or vinyl acetate; vinyl polymers, such for example as polyvinyl chloride, polyvinyl fluoride, polyacrylonitrile, and copolymers of acrylonitrile (preferably those prepared from monomer mixtures containing more than about 85% acrylonitrile); poly(tetramethyl - butadiene); polyamides such for example as polyhexamethylene adipamide, methoxymethylated polyhexamethylene adipamide, polytetramethylene sebacamide and polycaprolactam; polyesters, such for example as poly(ethylene terephthalate); polycarbonates; polyurethanes, e.g. as described in United States Patent Specification Nos. 2,731,445 and 2,731,446; polyethers, e.g. polyformaldehyde; polyureas; poly(alkylsulphones).

In addition to the polymers and copolymers disclosed above, graft and block copolymers are suitable for forming the plexifilaments to which a modifier may be grafted by the process of this invention.

Thus, the polymers useful for making the plexifilaments to be grafted by the process of this invention include those polymers which form homogeneous solutions at autogenous or higher pressures in a solvent or solvent mixture boiling at least $25^\circ C$. below the softening point of the polymer. Such solutions do not have to be homogenous at room temperature; it is usually required that a homogenous solution of the polymer

in the appropriate solvent exists at a temperature at least as high as the boiling point of said solvent or solvent mixture under autogenous or higher pressure.

- 5 Any organic compound, as defined above, may be employed as the modifying material which may be grafted to the plexifilament.

Among suitable unsaturated modifiers are hydrocarbons such as ethylene, propylene, styrene, α -methyl styrene, divinyl benzene, 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2-chloro-2,3-butadiene, isoprene, cyclopentadiene and chloroprene; acids such as maleic acid, crotonic acid, dichloromaleic acid, furic acid, acrylic acid, methacrylic acid, undecylenic acid, cinnamic acid; amides such as acrylamide, methacrylamide, N-methylolacrylamide, N-methyl-N-vinyl-formamide, N-vinyl-pyrrolidone, methyl substituted N-vinyl-pyrrolidone, vinyl - oxyethyl - formamide, methylene - bis - acrylamide, N - allyl - caprolactam; acrylate esters such as methyl acrylate, ethyl acrylate, benzyl acrylate, octyl acrylate, methyl methacrylate, butyl methacrylate, vinyl acrylate, allyl acrylate, ethylene diacrylate, diallyl itaconate, diethyl maleate, N,N-diethylaminosthyl methacrylate, dihydroxy-dipyrone; nitriles such as acrylonitrile, methacrylonitrile; acrylyl halides such as acrylyl chloride; vinylic alcohols such as allyl alcohol, furfuryl alcohol, 3-hydroxy-cyclopentene, dicyclopentenyl alcohol, tropolone; aldehydic compounds such as acrolein, methacrolein, crotonaldehyde, furfural, acrolein diethyl acetal; vinyl amines such as vinylpyridine, allyl-amine, diallyl-amine, vinyloxyethylamine, 3,3 - dimethyl - 4 - dimethyl - amino - 1 - butene, N,N - diacryltetramethyl - ene-diamine, N,N-diallyl-melamine, diamino-octadiene; quaternised amines such as tetraallyl ammonium bromide, vinyl trimethyl ammonium iodide, the quaternary methiodide of methylene - 3 - aminomethyl - cyclo - butane; vinyl esters such as vinyl acetate, vinyl salicylate, vinyl stearate, allyl formate, allyl acetate, diallyl adipate, diallyl isophthalate; vinyl ethers such as allyl glycidyl ether, vinyl 2-chloroethyl ether, dihydropyran, methoxy polyethyleneoxymethacrylate; vinyl halides such as vinyl chloride, vinyl fluoride, tetrachloroethylene, tetrafluoroethylene, 1,1-dichloro-2,2-difluoroethylene, vinylidene chloride, hexachloropropene, hexachlorocyclopentadiene, *p* - chlorostyrene, 2,5 - dichloro - styrene, allyl bromide, 2-bromo-ethyl acrylate, vinyl tetrafluoropropionate, 1,1,7-trihydroperfluoroheptylacrylate; isocyanate type compounds such as vinyl isocyanate, acrylyl isocyanate, allyl isothiocyanate; vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone; cyanides such as methacrylyl cyanide, allyl isocyanide; nitro compounds such as 2-nitropropene, 2-nitro-1-butene; phosphorus-containing vinyls such as diethyl vinyl phosphate, diphenyl vinyl phosphine oxide, 1-

phenyl-3-phosphacyclopentene-1-oxide, diallyl benzene phosphonate, potassium vinyl phosphonate, bis-chloroethyl vinyl phosphonate; also included are alkyl, aryl, aralkyl phosphonates, phosphites and phosphonates; sulphur containing vinyls including sulphonates, sulphonamides, sulphones, sulphonyl halides; thiocarboxylates, such as diallyl sulphide, ethylene-sulphonic acid, allyl-sulphonic acid, methallyl-sulphonic acid, styrene-sulphonic acid, 2-methylpropene-1,3-disulphonic acid, and salts and esters of the sulphonic acids; epoxy vinyls, such as butadiene oxide, glycidyl methacrylate.

Acetylenes such as phenylacetylene, acetylene dicarboxylic acid, propionic acid, propargylsuccinic acid, propargyl alcohol, 2-methyl-3-butyne-2-ol, and 2,2,3,3-tetrafluorocyclobutylvinylethylene may be used successfully.

In addition to compounds containing ethylenic unsaturation, it has been found that compounds can be grafted, according to the process of this invention, which are ordinarily regarded as non-polymerisable. By non-polymerisable is meant those compounds, free from aliphatic unsaturation, which do not polymerise by free radical initiation. It is believed that, owing to the efficiency of the high-energy radiation in producing free radicals, free radicals are produced simultaneously on the polymer substrates and on the saturated non-polymerisable compounds, whereupon grafting ensues. The preferred non-polymerisable compounds are those which have functional groups which are useful in modifying polymer properties. Thus, useful compounds include hydrocarbons, alcohols, acids, ethers, ketones, esters, aldehydes, isocyanates, sulphonates, mercaptans, thioethers, disulphides, nitriles, nitro compounds, amines, amides and halides. Typical of suitable alcohols are the alkanols such as methanol, ethanol, lauryl; and the polyols, such as glycerine, pentaerythritol, sorbitol, mannitol, and their partial esters. Diallyl ethers such as dimethyl, diethyl, and ethylmethyl ethers, and the glycol ethers, as well as the oxyalkylated ethers of partial esters of the polyols, such as the polyoxyethylene derivative of a fatty acid partial ester of sorbitol, are suitable. Mercaptans and thioethers analogous to the above may be used, as may also disulphides of a similar nature. As amines may be mentioned the alkyl amines such as methylamine, ethylamine, hexamethylene diamine and dodecylamine. The amides of these amines formed with acids such as formic acid, adipic acid, succinic acid, stearic acid and the like are useful; moreover the acids alone are often desirable modifiers. Halides within the preferred class include the alkyl halides such as chloromethane, chloroform, carbon tetrachloride, chloroethane, chloroethylene, dichlorodi-

fluoromethane, dodecafluoroheptyl alcohol and similar materials.

Of the non-polymerisable compounds, those organic compounds whose bonds are easily broken, as, for instance, chain transfer agents, are particularly preferred, since larger amounts of modifier are grafted with a given irradiation dose.

It is, of course, obvious that low molecular weight non-polymerisable modifiers are preferred when it is desirable to have the modifier penetrate into the plexifilament substrate, to make a bulk modification. It has been observed that modifiers with functional groups which have a swelling effect upon the polymer are usually especially effective in penetrating the substrate.

Polymeric modifiers are especially suitable when a surface coating is desired, since it is obvious that their ability to penetrate will be limited. When irradiating these compositions, it is believed that the coating is grafted by chemical bonds to the plexifilament surface. Therefore, the process of this invention gives a much more durable coating than those obtainable by prior art processes which require polymerisation initiators to cross-link the coating, and depend on mere physical bonds to retain the coating upon the polymer substrate. The polymeric modifiers are especially adaptable to the process of this invention, since relatively few bonds are needed to graft each large macromolecule to the substrate surface.

The process of this invention is suitable for washfast modification of plexifilaments, without destruction of their fibrous structure. These advantages are obtained primarily because the polymeric modifiers are applied in a relatively fluid state (e.g. from solutions of low viscosity) so that each filament is individually coated, and large excesses of the modifier are avoided. Excess amounts of modifier bond the fibrils of the plexifilament together, and may render it unfit for some uses; e.g. the plexifilament may no longer be dispersible. The preferred polymeric modifiers are those which are soluble or dispersible in aqueous solutions, although other solvents may be used in some cases. However, water is the preferred solvent because of its cheapness, availability, and freedom from hazards. Thus, such polymers as the polyether glycols, polypropylene ethers, polymeric alcohols, polymeric acids, polymeric amines, and polymeric amides are preferred. These compounds are useful, for example, in increasing moisture regain, antistatic effect, and wickability of those plexifilament substrates which otherwise are highly hydrophobic. Alternatively, water repellence can be improved by grafting hydrophobic polymeric materials, usually utilising a solvent other than water. Examples of such hydrophobic polymers are polytetra-

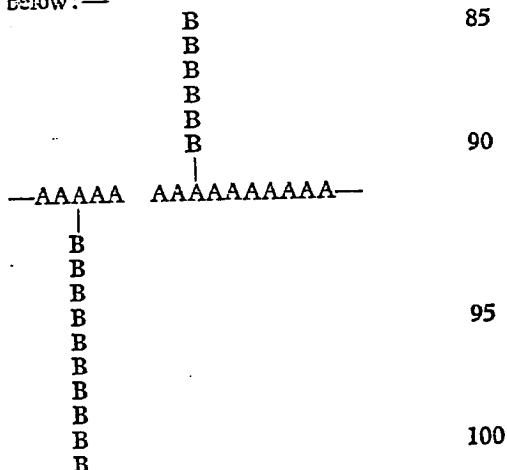
fluoroethylene, polyvinyl chloride, and polymeric esters.

The process of this invention produces a polymeric structure which has been termed a grafted polymer, that is, a polymer in which a modifying agent (polymerisable or unpolymerisable compound, or polymeric chain) is grafted by chemical bonds, usually as a side chain, to the parent polymeric substrate.

Conventional copolymers, consisting of monomer species A and B, have a random distribution along the backbone of the polymer molecule, and may be represented schematically thus:—

—AAABBABBBABAA—

The grafted polymer species with which one embodiment of this invention is concerned consists of a main chain of polymer A, and side chains of polymer B grafted thereto, represented below:—



The characteristic of this polymer type is that its gross properties remain predominantly those of the polymer (A) forming the molecular backbone. However, modifications can be produced by polymer (B) grafts, in most cases without loss of the original desirable properties. As an example, conventional copolymers usually have a lower melting point than those of either component, while grafted polymers usually retain the high melting point of the pure backbone component. The structure and preparation of some examples of this kind of polymer are discussed in a comprehensive review article by E. H. Immergut and H. Mark in *Makromolekulare Chemie* 18/19, 322—341 (1956).

It is obvious, of course, that when the modifier B is not homopolymerisable, single B units will be grafted to the polymer substrate A, producing another embodiment of the invention. Examples of such compounds are maleic acid, dodecafluoroheptyl alcohol, glycerol, and palmitic acid.

A third embodiment is that wherein the grafted modifier, B, is a preformed polymer (e.g. Carbowax, polyacrylic acid, polymeth-

acrylic acid). In this case, it is unlikely that any substantial amount of polymer B is grafted to A by free radicals generated on the ends of the B chain, as suggested by the structural formula above; more typically, bonding will occur between polymer A and some intermediate atom in the polymer B modifier.

The organic compound may be applied to the plexifilament as a liquid or liquid composition by immersion, padding, calendering, spraying, exposure to vapour condensation, or by other similar means. It is sometimes desirable to remove excess liquid by squeezing prior to the irradiation. Alternatively, the organic compound may be deposited upon the plexifilament by applying it as a solution and flashing-off the solvent.

As described previously, it is desirable that the modifier be applied to the substrate in a highly fluid condition; thus, application from solutions with a viscosity of the same order of magnitude as water are preferred. This permits the complete coating of each fibril of the plexifilament.

In its preferred embodiment, the process of the invention is directed to producing modifications throughout the bulk of the plexifilament substrate by using a modifier which, applied to the surface, penetrates therethrough; for modifiers which do not penetrate, modification is restricted to the surface. Thus, when the plexifilament is penetrated with the modifier prior to initiating the graft polymerisation, modification of the structure extends at least through a substantial proportion of the body of the final product. Increased contact time and agitation are helpful in increasing penetration. It is sometimes beneficial to carry out the soaking for penetration at elevated temperatures, at superatmospheric pressure or in the presence of swelling agents, dye carriers, or the like. However, elevated temperatures are to be avoided when using modifiers, such as strong acids, which may degrade hydrolysis-susceptible polymers. Minor amounts of wetting agents, surface active compounds, and the like are useful for improving penetration efficiency.

When it is desirable to limit penetration of the polymerisable composition to a zone near the substrate surface, this may be accomplished by reduced contact time or temperature, or use of modifiers with greater chain length. Alternatively, the shaped substrate may be exposed to the modifier for the time required to effect the desired depth of penetration, and further penetration stopped by freezing, for example with solid carbon dioxide. The combination may then be irradiated while frozen, and grafting will occur on subsequent warming.

Where the modifier is applied from a solution, water is usually the preferred solvent, but other liquids may be used such as alcohol, benzene, toluene, glycol, high boiling ethers

and the like; where high soaking or irradiation temperatures are used, a non-volatile solvent is often advantageous.

Flash-extruded plexifilament yarn, drawn or undrawn, is the preferred substrate to which the modifier is grafted. However the grafting step may be carried out on fabrics, on a fibre slurry, or even (less desirably) on the fibres in paper form.

In another embodiment of the process of the invention, which is only acceptable in some cases, the modifier may be dissolved in the spinning solvent along with the polymer, and the combination co-spun, grafting being initiated in a later step by exposing the plexifilaments to ionising radiation.

It is obvious, of course, that in this last embodiment the choice of modifiers which may be employed is limited, since modifiers must be avoided which, at spinning temperatures, degrade, cross-link or precipitate the polymer or themselves homopolymerise or decompose. Volatile modifiers may flash off with the solvent during spinning, or may be so incompatible with the polymer that no filaments are formed. For polymer-modifier combinations where these difficulties are not encountered, this embodiment will often provide acceptable products, and is useful especially when bulk modification is desired, using a modifier which when applied from outside will not penetrate the solid plexifilaments. It should be noted, however, that a major advantage of grafting to preformed plexifilament substrates is the large weight gain per unit radiation dose; the embodiment of the process just described foregoes this advantage.

The ionising radiation useful in the process of this invention must have at least sufficient energy to non-selectively break chemical bonds. This radiation is to be distinguished from ultraviolet radiation, which is effective in activating or ionising only such specific chemical bonds as are responsive to ultraviolet radiation of a given wavelength or wavelengths. It is often necessary to use an ultraviolet-photo-initiator in such reactions, so that light of available wavelengths will initiate the desired chemical reaction. In contrast, the ionising radiation used in this invention has more energy than is needed to break any chemical bond. Thus, this ionising radiation serves to activate polymer substrates so that chemical reactions are initiated with organic compounds, or, alternatively, to activate non-polymerisable organic compounds so they react with the polymer substrate.

In general, ionising radiation is preferred which has sufficient energy for an appreciable substrate thickness to be penetrated, and, in addition, for radiation absorption by the atmosphere to be low enough to make it unnecessary to operate in a vacuum. Such radiation has an energy of at least about 0.1 Mev. Higher energies are even more effective.

tive; the only known upper limit is imposed by available equipment.

The ionising radiation of the process of this invention is generally considered in two classes: Particle radiation, and electromagnetic radiation. Effects produced by these two types of radiation are similar, since in their interaction with matter, each generates secondary radiation of the other type. The

important consideration is that the incident radiation exceed the minimum threshold energy. Details of the mechanism of the interaction of high energy electrons with organic matter, including polymers, are not completely known, but the initial reaction is considered to be the absorption of energy by the valency electrons of the irradiated molecules in or near the path of the high energy electrons. The absorbed energy may be so great that some valency electrons will be shot off fast enough to ionise still other molecules. Some of the displaced electrons fall back to form neutral molecules and give up their energy as electromagnetic radiation, which in turn can be absorbed by other molecules and thus raise them to an excited stage. Further redistribution of the energy in the molecules results primarily in C—C bonds splitting off H atoms or molecules, producing free radicals or unsaturation.

The similarity of effect between the two types of radiation is thought to be due to the fact that an electron is ejected when an atom absorbs a quantum of high energy X- or gamma-rays; this electron has sufficient energy to eject electrons from other atoms in its turn, giving an effect corresponding to that of irradiation with an electron beam. Thus, the initial effect of high energy irradiation is to produce high energy electrons, which within the irradiated substrate produce free radicals. Consequently, the effects produced by particle and electromagnetic irradiation of equivalent energy are very similar, and differ only in the rate at which the effect is produced, which is a function of dose rate. The dose rate is a function of the equipment available to produce it, rather than an inherent limitation of the type of irradiation. Thus, with present day equipment, higher dose rates are obtainable with electron irradiation than are obtainable with X-rays of equivalent energy.

Although the fundamental particles differ from one another in size and charge, their mechanism of energy loss is essentially the same. Thus, their effect on chemical reactions is also similar. Although the neutron is not a charged particle it produces protons and gamma-rays which lose energy in the normal ways and consequently is effective in the process of this invention.

The heavier charged particles, like the electrons, undergo inelastic collisions with the bound electrons of atoms which they eject

to produce ions. Some of these ejected electrons may be sufficiently energetic to produce ionisations of their own. The energy of all these particles is used up in removing the bonded electron (i.e. in ionisation) and in producing excited atoms until all the electrons have become of such low energies that they can no longer produce ionisation and are captured to form negative ions. Neutrons do not produce ionisation directly, but knock out protons from the nucleus of the atoms they traverse. The chemical effects of fast neutrons are, therefore, almost wholly due to protons in exactly the same way as the effects of X-rays are produced by the ejected electrons. Unlike the other ionising radiations, however, the number of ionisations produced by neutrons depends largely on the nature of the elementary composition of the material through which the neutrons pass. The reason for this is that the transfer of energy between neutrons and protons does not depend on the atomic number but on other factors, such as chemical composition of the absorbing material.

Therefore, the high energy particle radiation effective in the process of this invention is an emission of highly accelerated electrons or nuclear particles such for instance as protons, neutrons, alpha particles, deuterons or beta particles, directed so that the said particles impinge upon the polymer bearing the organic compound. The charged particles may be accelerated to high speeds by means of a suitable voltage gradient, preferably at least 0.1 Mev, using for instance such devices as a resonant cavity accelerator, a Van de Graaff generator, a betatron, a synchrotron or a cyclotron, as is well known to those skilled in the art. Neutron radiation may be produced by bombardment of selected light metal (e.g. beryllium) targets with high energy positive particles. In addition, particle radiation suitable for carrying out the process of the invention may be obtained from an atomic pile, or from radioactive isotopes or from other natural or artificial radioactive materials.

Similarly, ionising electromagnetic radiation useful in the process of this invention is produced when a metal target (e.g. gold or tungsten) is bombarded by electrons possessing appropriate energy. Such energy is imparted to electrons by accelerating potentials in excess of 0.1 Mev. Such radiation, conventionally termed X-ray, will have a shorter wavelength limit of about 0.01 Angstrom units (in the case of 1 Mev) and a spectral distribution of energy at longer wavelengths determined by the target material and the applied voltage. X-rays of wavelengths longer than 1 or 2 Angstrom units are attenuated in air, which puts a practical long wavelength limit on the radiation. In addition to X-rays produced as indicated above, ionising electromagnetic radiation suitable for

carrying out the process of the invention may be obtained from a nuclear reactor ("pile") or from natural or artificial radioactive material, for example cobalt 60. In all of these latter cases, the radiation is conventionally termed gamma-rays. While gamma radiation is distinguished from X-radiation only with reference to its origin, it may be noted that the spectral distribution of X-rays is different from that of gamma-rays, the latter frequently being essentially monochromatic, which is never the case with X-rays produced by electron bombardment of a target.

To be efficient in the practice of the present invention, it is necessary that the high energy particles have sufficient velocities to permit penetration of several layers of material. Although an energy of about 50 ev is enough to initiate the grafting reaction, energies of at least 0.1 Mev are preferred for efficient penetration. The velocity required will depend on the nature of the particle and also on the nature of the substrate to a certain extent. Electrons accelerated by a potential of a million volts will effectively penetrate a thickness of polyhexamethylene adipamide fabric of about 0.25 cm. A more universal measure of penetration for all substrates is in units of grams penetrated per square centimetre irradiated. Thus, 2 Mev electrons will effectively penetrate 0.7 gm./cm² of any shaped article, while 1 Mev electrons are effective for 0.35 gm./cm².

As stated previously, there is no known upper limit to the particle energy, except that imposed by present day equipment. Thus, energies equivalent to 24 Mev to 100 Mev may be used.

As a guide in using other charged particles which have been shown to be effective in grafting, the following table shows particle energies required to give penetration equivalent to 0.1 Mev electrons.

TABLE

Particle	Accelerating potential, Mev
Electron e ⁻	0.1
Proton H ⁺	3.0
Deuteron D ⁺	4.0
Alpha He ⁺⁺	12.0

It should be recognised that the heavier charged particles are especially adapted to creating surface effects, since they have a lower penetration at a given energy. In situations where surface effects are paramount, it is not necessary that the shaped article be completely penetrated by the high energy particle and lower accelerations may be employed. Under those conditions, if the surface effect is to be applied to both sides of the article, it will obviously be necessary to expose each of the surfaces to the particle radiation. This can be done by simultan-

eously bombarding both sides of the shaped article or alternatively by subjecting each side to the single source of irradiation during different runs.

High energy particle radiation has special utility for grafting modifiers to thin substrates such as plexifilaments. The required irradiation doses with present day electron accelerators, such as exemplified herein, are attained rapidly, in a matter of seconds, thus promoting a high rate of throughput.

In comparison, high energy electromagnetic radiation in short wave lengths is highly penetrating, and hence readily lends itself to treating massive substrates. When grafting to the preferred substrates of this invention, this type of radiation is especially useful for irradiating materials present in multiple layers. For example, bolts of fabric, yarn packages, and bales of staple fibre formed from the plexifilaments may be irradiated as a single unit.

As an illustration, X-rays generated by electrons of 2 Mev have adequate penetration for polymer samples several inches in thickness. Lower energy (longer wavelength) X-rays are, of course, less penetrating so that it may be necessary to reduce the thickness of material to be treated simultaneously. The very long (soft) X-rays, because of their low penetration, may be especially effective in producing surface effects.

Although the treatment can be carried out using conventional X-ray equipment, the use of radioactive isotopes such as cobalt 60 is especially economical. Radiation from waste fission products, with particle irradiation screened off if desired, is also effective and offers an opportunity to utilise an otherwise useless waste product.

In determining the optimum dose of irradiation for any particular combination, both the nature of the organic compound and the nature of the substrate must be considered. For example, for vinyl monomers which are readily graftable, and polymer substrates that are readily activated by ionising radiation, it appears that the greater part of the minimum irradiation dose is required to consume the inhibitor (including oxygen) which may be present in the vinyl monomer. After that is done, relatively low additional doses will produce enough radicals to initiate graft polymerisation. For readily graftable combinations of this type, a high polymerisation rate is observed. Thus, the extent of irradiation-induced graft polymerisation can be increased by increasing radiation dose, post-irradiation time, or both. For instance, if a polymer plexifilament soaked in acrylic acid solution is irradiated with a dose of 0.06 Mrad, and the irradiated sample is kept in contact with the acrylic acid solution for 1 hour at room temperature, a large amount of the acid is grafted. In contrast, with the same dose, if the mono-

mer is removed from the sample immediately after irradiation (e.g. by a water extraction), only one-third as much acrylic acid is grafted. Therefore, for polymerisable vinyl compounds and readily graftable polymer substrates, a very small dose is required; thus, a minimum dose of 5000 rads (0.005 Mrad) initiates a significant amount of grafting.

When unsaturated compounds which are not homopolymerisable (e.g. maleic acid) are used as the modifier, in combination with readily graftable substrates, doses of 0.1 Mrad are required to initiate appreciable grafting. When non-polymerisable organic compounds or saturated polymeric modifiers are used, a minimum dose of 1 Mrad should be employed. Radiation doses below the minimum specified fail to initiate beneficial amounts of grafting within a practical length of time. This is because the life of free radicals produced by the irradiation depends on a balance between competing (i.e. non-grafting) reactions and those which produce grafting. It is obvious, of course, that even lower doses may be used in completely inhibitor- and oxygen-free systems, or if irradiation-initiation of grafting is supplemented by a chemical initiator.

Although the minimum doses specified are effective, higher dosages may be used and are usually highly beneficial. Dosages so high that substantial degradation of the shaped substrate occurs must obviously be avoided. High doses cross-link some polymers, which may sometimes be undesirable. In general, plexifilaments produced from polyacrylonitrile, polyhexamethylene adipamide, polyethylene terephthalate and polyethylene may be irradiated to a dosage as high as 100 Mrad. However, it is preferred that the dosage applied to these substrates should not exceed about 50 Mrad. Polyvinyl halide substrates generally should not be exposed to a dose greater than 25 Mrad.

The distinction between "available irradiation" and "dose" should be recognised. The 2 Mev Van de Graaff electron accelerator used in many of the examples given below, operated as described, provides 12.5 watt seconds of irradiation per cm.² of substrate per pass. For thin, organic polymer substrates (i.e. having a thickness of a few millimetres or less), the dose (energy absorbed) is about 1 Mrad. Since much of the energy of the incident beam is not absorbed, several (fabric) samples may be irradiated simultaneously, each absorbing a dose of 1 Mrad. Thicker substrates may absorb substantially all of the incident radiation energy, but the dose absorbed in the layers more distant from the electron source may not be sufficient to form a useful number of free radical sites.

Once free radicals are produced on the carbon atoms of the polymer chain in the presence of a vinyl monomer, vinyl polymerisation is initiated, and polyvinyl chains grow

from the initiating sites. However, it has been observed that the life of free radicals is many times greater than has been found in vinyl polymerisations carried out in solution or emulsions. For this reason, at a given radiation dose, the yield of polymer grafted to the shaped substrate is much greater than would be obtained, for example, if the substrate polymer were dissolved in the vinyl monomer and the solution irradiated.

The average molecular weight of the polymer chains grafted to the substrate (at a given constant weight gain) may be controlled by adjusting the radiation dose. It may also be adjusted by controlling chain transfer to the substrate polymer, e.g. by changing grafting temperatures, or modifying the substrate polymer by incorporating copolymer components which are more (or less) susceptible to chain transfer. Similarly, the molecular weight distribution of these chains may be adjusted. By controlling the number, length and length distribution of grafted chains, the effect produced by a given grafting agent may be modified.

It has been observed that irradiation of the modifier-treated shaped substrate in the presence of air or moisture may occasionally cause some degradation; such adverse effects can be avoided by employing an atmosphere of inert gas around the article while it is being irradiated. Alternatively, a satisfactory and simpler approach is to wrap the sample in a material which is substantially impervious to air and water, for example polyethylene film or aluminium foil, thus limiting the quantity of air or moisture contacting the sample. Complete exclusion of oxygen is not required, although it may contribute to grafting efficiency when using a vinyl monomer. The nature of the wrapping material is not critical, provided it is substantially impervious to air and moisture, when required, and is readily penetrated by the radiation.

It is within the scope of this invention to include in the combination to be irradiated materials which may have a protective or antioxidant effect so as to prevent radiation degradation of either modifier or substrate or both. Compounds of this type are cysteine, carbon and polyethylene glycols. It is also within the scope of this invention to include in the combination to be irradiated materials which absorb radiation and transmit the energy thus absorbed to the modifier or the organic polymeric material or both, so increasing the efficiency with which the radiation is utilised. Compounds with this property are somewhat similar to sensitizers in photography, except that in this case useful materials absorb high energy radiation and emit the energy in a lower or more usable range. Phosphor screens containing calcium tungstate, zinc sulphide or metallic lead are useful for this purpose. The phosphor materials may be used

as plates contacting the material being treated, or may be incorporated in the modifying agent or even be coated on or dispersed in the plexifilament.

5 The irradiation may be effected over a wide range of temperatures. However, a low temperature decreases the tendency toward oxidation. Since the absorption of particle radiation frequently causes a temperature increase in the range of about 2° C. for each 10 Mrad absorbed, if high tube current is employed so that radiation absorption is complete within a short time interval, it is usually advisable to provide means to remove the 15 heat generated to avoid injury to the sample. The use of solid carbon dioxide to maintain a cold atmosphere is very satisfactory for this purpose. In general, a higher temperature increases the speed with which bonding 20 occurs, thus making possible a higher throughput with a given piece of equipment at a constant radiation dosage. Temperatures ranging from -80° C. or below up to the melting point of the polymer substrate may be employed but more efficient grafting is often 25 noted when irradiation temperatures are in the range of 100 to 160° C.

In general, for the greatest weight of modifier to be grafted for a given dose, the organic 30 compounds are applied to the substrate as liquids or solutions of relatively high concentration. Such procedure provides the maximum opportunity for the organic compound to be bombarded by the high energy particle. 35 In some cases the concentration of the organic compound on the substrate will noticeably affect the final properties.

The plexifilaments may contain additives such as pigments, antioxidants, fillers or polymerisation catalysts. After the irradiation, 40 the product may be after-treated. Frequently a certain amount of decomposition occurs at the surface, the products of which are readily removed by washing in detergent. In other 45 after-treatments, the article may be dyed, bleached, hot or cold drawn, chemically reacted, or given coatings of lubricants, sizes, or the like or other similar treatments.

The grafting reaction may be carried out as 50 a batch operation or continuously, either supplementary to or, preferably, as a separate operation from the flash-spinning.

The process of the invention is valuable in 55 creating both surface and bulk effects upon the plexifilaments. It may be employed upon textile to effect softness, resilience, tendency to shrink, static propensity, resistance to hole-melting, pilling, hydrophilicity, wickability, and the like. It is useful in changing 60 such properties as tenacity, elongation, modulus, creep, compliance ratio, work recovery, tensile recovery, decay of stress, wet properties, high-temperature properties, abrasion and wear resistance, moisture regain, flex life, hydrolytic stability, heat-setting properties, boil-

off shrinkage, dry-cleaning properties, heat stability, light durability, zero strength temperature, melting point, soilability, ease of soil removal, laundering properties, wash-wear 70 properties, liveliness, crease resistance, crease recovery, torsional properties, hysteresis properties, fibre friction, dyeability, (depth, rate, permanence and uniformity), printability, washfastness of dyes or finishing treatments 75 using for example resins or ultraviolet absorbers, handle and drape properties, (stiffening or softening), heat-yellowing, snag resistance, elasticity, density, ease in textile processability, solubility (e.g. to cause insolubilization or an increase in solubility), bleachability, 80 surface reactivity, delustering action, drying properties, fabric life, crimpability, stretchability, fabric stabilisation, compressional resilience (for rugs), thermal and electrical conductivity, transparency, light transmittance, air 85 and water permeability, fabric comfort, felting, ion exchange properties, germicidal properties, adhesion, over-all appearance and combinations of these as well as others.

In addition to the above modifications which 90 it may be desirable to effect in plexifilaments for textile uses, there are other modifications which are particularly useful when the plexifilaments are used in papers. Typical modifications improve dispersibility, ion exchange 95 properties, strength (wet or dry), tear resistance, durability, burst resistance, vapour permeability, dyeability, abrasion resistance, fold resistance, light durability, heat durability, flame resistance, and many other properties. 100

The grafted products of this invention may be used in a wide range of compositions with Kraft or other pulps to make useful paper products. In addition, the grafted products 105 are suitable for making 100% synthetic fibre paper. Especially useful compositions are obtained by blending acid-grafted and unmodified plexifilaments.

The plexifilaments of the present invention are particularly suitable as binders for other 110 fibrous materials. The plexifilament particles can be bonded intimately to a stress-bearing component, preferably of a material melting higher than the plexifilaments. Thus the final bonding conditions depend almost 115 entirely on the nature of the plexifilaments. Typical stress-bearing components are: Kraft and other cellulosic pulps, cellulosic fibres, glass, man-made fibres such as those of cellulose acetate, rayon, polyesters, polyamides, 120 polyethers, polyvinyl chloride, polyureas, polyurethanes, acrylonitrile polymers, poly(tetrafluoroethylene), polysulphonamides, polyphosphonamides, hydrocarbon polymers of the linear or branched variety, and copolymers 125 and blends of polymers as well as graft copolymers.

Of course the stress-bearing fibres can vary widely in their denier range. The fibre denier will be selected to suit the intended end use 130

for the sheet product made. The fibres can be cut into staple lengths, which also can vary widely with the desired end product, but generally fall within the range of from 1/8" to about 2".

Any of the well-known raw cellulosic materials can be used to prepare the cellulose-containing papers. These sources include wood, cotton, and linen rags, cotton linters and staple, bagasse, bamboo, manila rope, esparto, cereal straws, flax, straw, bast, ramie, sisal, hemp, and waste paper. Of these, the pulps which are capable of making strong sheets, such as Kraft, manila, bleached sulphite pulp and bleached sulphate pulp are preferred.

A grafted plexifilament pulp can be de-watered to a composition containing 20% or more of solids suitable for shipping and re-dispersing. This pulp can be diluted to the proper level for the formation of homo-sheets, or it can be blended with other pulps of stress-bearing fibres to form hetero-sheets of any desired characteristics. The pulp can also contain or can be blended with additives as listed earlier but, for good sheet formation in the processing steps, at least about 3% of grafted plexifilaments based on the total content of solids is recommended. Generally sheets containing at least about 5% grafted plexifilaments are preferred.

These sheet products are useful in many applications. They can be made of various thicknesses or basis weights, the latter usually being within the range of from 0.5 to 30 oz/yd². Such sheets include products which would be considered lightweight papers as well as heavy structures similar to cardboard. An important use for pressed products of heavy basis weight is in the formation of containers, such as those used for butter, cheese and milk. The sheets can be used in many packaging applications where cellulosic paper bags or perforated polyethylene films are now being used, particularly for packaging goods which are stored or handled occasionally out of doors. Such bagging materials include mail bags, cement bags and vegetable containers, in other words, uses where wet strength is of importance. In such end uses, the products of the invention would replace much heavier constructions such as impregnated fabrics, coated cardboard, and wooden boxes. Thinner sheets containing grafted plexifilaments may be used as battery separators and as electrical papers in condensers, particularly when made entirely from synthetic ingredients. They may also be used for wrapping electric cables. In general, such products have high electrical insulation values, good thermal stability, very high wet strength, exceptionally good hot-wet properties, good heat insulation values, and many other valuable properties. The structures containing cellulosic components are superior in wet strength to sheet pro-

ducts made entirely from cellulosic materials when compared to one another calculated on the same basis weight. The sheet products made entirely from grafted synthetic polymers have a very favourable cost-performance ratio when factors such as dry and wet strength, tear strength, burst strength, electrical and heat insulation, corrosion, and influence on micro-organisms are involved.

Other articles which can be made advantageously from the above compositions, include anode bags, high performance printable papers, foil papers, filter papers and other filter media, absorbent products, low cost tarpaulins, construction covers, parachutes, laminates, paper dishes, utility clothing, inner liners and head liners.

The paper-making process may, of course, be carried out continuously on conventional paper machinery. Although dispersing agents are usually unnecessary in the acid-grafted plexifilamentary polymer slurry, they may be included without harmful effect. Other conventional additives may also be employed, such as sizes and fillers.

In the following examples all "parts" are by weight, and compositions are given in parts by weight or weight percent, unless otherwise noted.

The irradiation in many of the examples is carried out using a Van de Graaff electron accelerator with an accelerating potential of 2 million electron volts (Mev) with a tube current of 250 to 290 microamperes. Samples to be irradiated are placed on a conveyor and traversed back and forth under the electron beam at a distance of tube window to sample of 10 cm. The conveyor speed is 40 inches per minute. At the sample location the irradiation intensity is 12.5 watt sec./cm.² of sample, which is approximately equivalent to an available dose per pass of one Mrad.

Radiation dosages are given in units of "Mrad" (millions of rads), a "rad" being the amount of high energy radiation of any type which results in an energy absorption of 100 ergs per gram of water or equivalent absorbing material.

The static propensity of the fabric is indicated in terms of direct current resistance in ohms per square, measured parallel to the fabric surface, at 78° F. in a 50% relative humidity atmosphere. High values, reported as the logarithm (to the base 10) of the resistivity (log R) indicate a tendency to acquire and retain a static charge. A meter suitable for this determination is described by Hayek and Chromey, American Dyestuff Reporter, 40, 225 (1951).

Wickability as given in the examples is determined by placing a drop of water upon the fabric, and measuring the diameter of the wet spot after a standard time interval of

60 seconds. Alternatively, especially useful where decreased wickability is obtained, is a determination of the length of time required for a drop placed upon the fabric to disappear by soaking into the fabric.

- 5 Crease recovery is evaluated by crumpling a fabric in the hand, and observing the rate at which it recovers from this treatment. Wet crease recovery indicates the rate and extent of disappearance of creases from the crumpled fabric when it is wetted. Numerical values are obtained using the Monsanto Crease Recovery Method, described as the "vertical strip crease recovery test" in the American Society for Testing Materials Manual, Test No. D1295-53T. In determining wet crease recovery by this method, the specimens are soaked for at least 16 hours in distilled water containing 0.5% by weight of "Tween 20" ("Tween" being a Registered Trade Mark), a polyoxyalkylene derivative of sorbitan monolaurate, a wetting agent marketed by the Atlas Powder Company, Wilmington, Delaware. Immediately prior to testing, excess water is removed from the test fabrics by blotting between layers of a paper towel. Results are reported as percent recovery from a standard crease in 300 seconds.

EXAMPLE I

- 30 13 parts of linear polyethylene of melt index 0.5 and 87 parts of methylene chloride are charged to an autoclave, and are heated for 4 hours at 190—195° C. with stirring. The autogenous pressure is about 500 psi. Following the heating-dissolving step, a gate

valve at the bottom of the autoclave is opened and the solution is flash-extruded through an extrusion orifice which is 86 mils in diameter and 86 mils long. The flash-spun product is a plexifilament structure characterised by a plurality of fibrils which unite and separate at random longitudinal and cross-sectional intervals through the strand to provide a three-dimensional unitary network or web in which all the elements are integral with each other. Thus, it resembles very closely a staple fibre yarn without loose ends.

A portion of the as-spun yarn is drawn three fold while traversing a bath of ethylene glycol heated to 130—133° C. Fabrics are woven from the undrawn yarn, which has a denier of 700 to 1100, and from the drawn yarn, which has a denier of 200 to 300.

Portions of these fabrics are treated as indicated in Table I by soaking in acrylic acid solution for a period of 2 hours at room temperature; the fabrics, still wet with the treating solution, are sealed in polyethylene bags, and are irradiated to a dose of 2 Mrad, using 2 Mev electrons as described hereinabove. After irradiation, the fabrics are scoured two times in methanol on a steam bath, followed by rinsing in hot distilled water at 70° C., followed in turn by treatment for 40 minutes in a 2% sodium carbonate solution at 70° C. The sodium carbonate treatment forms the sodium salt of the grafted acrylic acid. Excess sodium carbonate is removed by rinsing in hot water at 70° C. The weight gain for each sample is also indicated in Table I.

TABLE I

	Sample	Yarn	Treating solution	Wt. gain, %
75	A	Undrawn	20% acrylic acid in heptane	24.5
	B	Drawn	" " " "	17.2
	C	"	30% " " " "	32.8
	D	Undrawn	20% " " " water, 0.1% sodium salt of lauryl alcohol sulphate	5.6

- 80 Fabric tests upon sample C show that it is highly resistant to hole melting. For example a lighted cigarette cannot be pushed through the fabric, and the fabric is still pliable after cooling. Fabric from unmodified polyethylene melts immediately. The sodium acrylate-grafted fibre does not break when held directly over a lighted cigarette under considerable tension whereas an unmodified yarn breaks immediately under the same conditions. In addition, the modified fabric has increased dyeability, improved hand, and better dry and wet crease recovery.

EXAMPLE II

- 95 A second batch of yarn is prepared as in Example I, starting with a 13% solution of the linear polyethylene of melt index 0.5.

When the polymer is dissolved, the autoclave pressure is increased to 650 psi, using nitrogen from a pressure cylinder. The yarn is flash-spun as before, except that, prior to extrusion, the solution is filtered through a series of stainless steel screens. The fibre has a tenacity of about 1.3 gpd.

About 20 g. of the undrawn fibre prepared as described above is placed in a 1 gallon polyethylene bag containing 400 ml. of an 8% solution of acrylic acid in heptane. The fibre is soaked for 2 hours at room temperature, and then the bag containing the solution and fibre is irradiated in two passes (once from each side) to a total dose of 2 Mrad.

The irradiated fibre is washed in cold methanol, then in hot methanol, followed by rinsing in distilled water at 70° C. The

grafted fibre is then heated for 40 minutes in 5% aqueous sodium carbonate at 70° C., followed by two rinses in hot distilled water to remove excess sodium carbonate. The fibre is then dried, and the weight gain, due to grafted sodium acrylate, is found to be 58.5%.

The grafted plexifilament is cut into pieces approximately $\frac{1}{4}$ " long, which are then stirred briefly in a Waring Blendor with sufficient distilled water to form a 1% suspension without use of dispersing agent or thickener. An equal weight of Kraft cellulose paper pulp is added, and is dispersed in the water. The dispersion is then diluted to make a suspension containing 0.25% by weight of total fibre, and paper is formed by depositing the furnish on a 100-mesh screen to make a hand sheet. The sheet is removed from the screen, and is dried at 110° C., allowing shrinkage to take place. The sample is then calendered in a press at 150° C. and 600 psi. for 1 minute. The sample is then tested with the results shown in Table II, using a sheet prepared from Kraft pulp as a control.

TABLE II
Sample

Control

Composition, parts:—

Polyethylene fibre	50	0
Kraft pulp	50	100

Tensile strength (1) (lb/in/oz/yd ²)	13.3	12.8
Frag. energy (2) kg/m	0.360	0.085

Water vapour permeability (3) g/m ² /24 hr.	5.0	890
Abrasion resistance, cycles (4)	120,000	590

M.I.T. Fold endurance, cycles (5)	421,000	1600
--------------------------------------	---------	------

(1) Tensile strength measured using an "Instron" Tensile Tester ("Instron" is a Registered Trade Mark)		
(2) Determined on the Frag Tester, sold by the Testing Machine Co. NY., New York.		

(3) Permeability measured using Thwing Vapometer cup		
(4) Tabor abrasion test		
(5) TAPPI Standards T-423-M-50.		

(1) Tensile strength measured using an "Instron" Tensile Tester ("Instron" is a Registered Trade Mark)		
(2) Determined on the Frag Tester, sold by the Testing Machine Co. NY., New York.		

(3) Permeability measured using Thwing Vapometer cup		
(4) Tabor abrasion test		
(5) TAPPI Standards T-423-M-50.		

(3) Permeability measured using Thwing Vapometer cup		
(4) Tabor abrasion test		
(5) TAPPI Standards T-423-M-50.		

These results show that the grafted polyethylene filaments, when added to Kraft pulp, yield a paper which is stronger than 100% Kraft, has greatly improved energy absorption (Frag energy), which is a measure of a resistance to bursting when a bag containing heavy articles is dropped, and in addition is highly resistant to permeability to water vapour, to abrasion and to repeated folding.

Although in this example a 60% graft of sodium acrylate to the polyethylene fibre is employed, other amounts are also suitable. For example, from 10 to 120% or more produces desirable modification. Other ions

may also be used to form the salt of the acrylic acid graft, although sodium ion is preferred.

Many other unsaturated organic acids are useful in modifying addition polymer filaments to improve their utility, for example for making paper. Thus unsaturated monocarboxylic acids such as methacrylic acid are suitable; for some purposes, difunctional acids such as maleic and fumaric acids may be employed, although acids which are not homopolymerisable may require an excessive radiation dose. In addition, sulphonic acids such as styrene sulphonic acid and ethylene sulphonic acid are suitable for special purposes. It may sometimes be desirable to graft the acid as the preformed salt, e.g. as sodium acrylate, or sodium styrene sulphonate.

EXAMPLE III

The irradiation grafted polyethylene plexifilament of Example II is cut into $\frac{1}{4}$ " pieces, slurried in soft water to a consistency of 0.5% and subsequently beaten in a Waring Blendor at a 1% solids consistency for 2 minutes without the use of a detergent. A hand sheet is prepared from the polyethylene plexifilaments alone. The wet hand sheet is removed from 100-mesh 8"×8" screen, dried at 110° C. in an oven and subsequently pressed at 150° C. and 60 psi. for 60 seconds. The sheet has a basis weight of 2.35 oz/yd², a tensile strength of 13.8 lb/in/oz/yd² of which it retains 5.1 lb/in/oz/yd² when wet, and a tongue tear strength of 0.1 lb/oz/yd². A Kraft paper sheet control is employed in observing the properties reported in Table III.

TABLE III

Sample

Control

Frag energy kg/m	0.94	0.08
Water vapor permeability g/m ² /24 hrs.	5	700

Water resistance (time in sec. for water to permeate)	1200	2
---	------	---

Water resistance (time in sec. for water to permeate)	1200	2
---	------	---

Water resistance (time in sec. for water to permeate)	1200	2
---	------	---

Water resistance (time in sec. for water to permeate)	1200	2
---	------	---

Water resistance (time in sec. for water to permeate)	1200	2
---	------	---

Water resistance (time in sec. for water to permeate)	1200	2
---	------	---

Water resistance (time in sec. for water to permeate)	1200	2
---	------	---

Water resistance (time in sec. for water to permeate)	1200	2
---	------	---

Water resistance (time in sec. for water to permeate)	1200	2
---	------	---

Water resistance (time in sec. for water to permeate)	1200	2
---	------	---

Water resistance (time in sec. for water to permeate)	1200	2
---	------	---

Water resistance (time in sec. for water to permeate)	1200	2
---	------	---

Water resistance (time in sec. for water to permeate)	1200	2
---	------	---

EXAMPLE IV

A 0.98 g. sample of flash-spun linear polyethylene plexifilament, prepared as in Example II, is soaked in a solution of 4 ml. of acrylic acid and 36 ml. of heptane overnight and irradiated to a dosage of 2 Mrads under a Van de Graaff electron generator while still in the soaking solution. The sample is washed in methanol and then in a 2% sodium carbonate solution at 85° C. for 45 minutes followed by rinsing and drying. The weight gain is 107%. When a sample of melt spun undrawn linear polyethylene is treated under similar conditions the weight gain is only 7%.

EXAMPLE V

A sample of flash-spun polyethylene plexifilament is soaked overnight in 13 ml. of dis-

tilled N-vinylpyrrolidone and 28 ml. of methanol and then irradiated as in Example IV. The sample is washed in distilled water at 85° C. for 45 minutes and rinsed. After drying the weight gain is 16.8% compared with 0.5% for melt spun linear polyethylene treated in a similar manner.

The grafted plexifilament is rapidly and deeply dyeable, whereas the melt-spun control is almost undyeable.

EXAMPLE VI

Flash-spun polyethylene plexifilament is soaked overnight in 20 ml. of acrylonitrile and 20 ml. of heptane and irradiated as in Example IV. The sample is washed in methanol and in dimethylformamide on a steam bath, rinsed in water and dried. The weight gain for the flash-spun plexifilaments is 23.7% compared with 3.8% for a corresponding melt-spun material.

The grafted plexifilaments show improved weather resistance compared with a melt-spun control and with the ungrafted flash-spun polyethylene plexifilaments.

EXAMPLE VII

Flash-spun polyethylene plexifilament is soaked in 20 ml. of distilled methyl acrylate and 20 ml. of heptane overnight and irradiated as in Example IV. The sample is washed in hot methanol and in hot methyl ethyl ketone. The graft weight gain is 50% compared with 17% for the melt spun polyethylene yarn.

EXAMPLE VIII

A flash-spun polyethylene plexifilament sample is soaked overnight in 20 ml. of distilled styrene and 20 ml. of heptane and irradiated for a dosage of 2 Mrads. The sample is washed in benzene at 60° C. and dried. The weight gain is 60.9% compared with 13% for a corresponding melt-spun sample.

EXAMPLE IX

30 g. of isotactic polypropylene (melt index 0.8) is charged to a 300 ml. autoclave along with 120 ml. methylene chloride. The autoclave is sealed and the mixture is heated to 185° C., dissolving the polymer. The solution is then flash-spun under autogenous pressure through a spinneret orifice 28 mils in diameter by 23 mils long. A plexifilamentary fibrous yarn is obtained, having a total denier (not drawn) of 230 to 330.

11 g. of the flash-spun polypropylene plexifilaments are soaked in a solution of 24 ml. of acrylic acid and 276 ml. of heptane for 2 hours, and then irradiated to a dosage of 2 Mrads. After washing successively in methanol and 2% sodium carbonate solution at 85° C. for 45 minutes and rinsing, the weight gain is 54.5%. A sample of melt spun material treated under similar conditions shows a weight gain of only 8.4%.

EXAMPLE X

10 g. of flash-spun polypropylene modified with sodium acrylate as in Example IX is cut to $\frac{1}{4}$ " lengths and is beaten in a Valley beater with 40 g. of Kraft pulp to a Schopper Riegler freeness of 350. Papers are prepared from this slurry in a sheet mould box by pouring 593 ml. of the slurry with 1 litre of water into the box and applying a vacuum. The sheet is then couched onto a blotter and dried in an oven without tension. The paper is pressed at 150° C. for 1.5 minutes at 80 psi.

The properties of the paper are listed in Table IV, along with the Kraft paper of Example II for comparison.

TABLE IV

	Sample	Control
Composition parts:—		
Grafted polypropylene	20	0
Kraft pulp	80	100
Tensile strength (lb/in/oz/yd ²) (dry)	11.2	12.8
Water vapour permeability g/m ² /24 hr.	27	890

In addition, the test paper was more resistant to bursting under impact load, to folding and to abrasion.

WHAT WE CLAIM IS:—

1. A plexifilament (as hereinbefore defined) of a grafted polymer (as hereinbefore defined).

2. A plexifilament according to Claim 1, in which the strand comprises a continuous plexus of fibrils, longitudinally oriented and integral with each other, and substantially free of loose ends.

3. A plexifilament according to Claim 2, in which the strand is substantially free of both tunnels and cavities.

4. A plexifilament according to any of Claims 1—3, in which the polymeric "backbone" of the grafted polymer is an addition polymer.

5. A plexifilament according to Claim 4 in which the polymeric "backbone" is a linear polyethylene.

6. A plexifilament according to any of the preceding claims, in which the grafted part of the grafted polymer is derived from an ethylenically unsaturated organic acid.

7. A plexifilament according to Claim 6, in which the organic acid is acrylic acid or methacrylic acid.

8. A plexifilament according to Claim 6 or 7, in which the organic acid is in the form of a salt thereof.

9. A plexifilament according to Claim 1 substantially as hereinbefore described.

10. Process for producing a plexifilament as claimed in any of the preceding claims, which comprise subjecting a plexifilament formed from a synthetic organic fibre-forming polymer to ionising radiation while it is in intimate

contact with an organic compound (as hereinbefore defined).

11. Process according to Claim 10, in which the plexifilament is formed from a linear polyethylene. 5
12. Process according to Claim 10 or 11, in which the organic compound is an ethylenically unsaturated organic acid.
13. Process according to Claim 12, in which the acid is acrylic or methacrylic acid. 10
14. Process according to Claim 12 or 13, in which, after the irradiation and the grafting of the acid to the initial plexifilament, the acid groups in the resulting grafted polymer are converted into salt groups. 15
15. Process according to Claim 14, in which the acid groups are converted into sodium salt groups.
16. Process according to any of Claims 10—15, in which the energy of the ionising radiation is at least 0.1 Mev. 20
17. Process for producing a plexifilament claimed in any of Claims 1—9 substantially as described in any of the foregoing Examples I, II and IV—IX. 25
18. Process for producing a plexifilament claimed in any of Claims 1—9 substantially as hereinbefore described.
19. Plexifilaments of grafted polymers obtained by a process claimed in any of Claims 10—18. 30
20. Fabrics and paper made from or containing plexifilaments claimed in any of Claims 1—9 or 19.

J. A. KEMP & CO.,
Chartered Patent Agents,
9, Staple Inn, London, W.C.1.

Reference has been directed in pursuance of section 9, subsection (1) of the Patents Act, 1949, to Patent No. 820,120.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1962.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

THIS PAGE BLANK (USPTO)
